



A Honeywell Company

Trace Metals in Organics by ICP-OES

UOP Method 389-15

Scope

This method is for determining the concentrations of aluminum (Al), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), palladium (Pd), phosphorus (P), platinum (Pt), potassium (K), sodium (Na), strontium (Sr), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn) in organic matrices such as crude petroleum, asphalts, vacuum tower bottoms, vacuum gas oils, atmospheric gas oils, diesel and jet fuels and their blending components, pyrolysis oils, and fatty acid derivatives by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The lower limits of quantitation for the above elements, except palladium, are listed in Table 1 (see *Note*).

Table 1
Lower Limits of Quantitation, mg/kg (mass-ppm)

Al	0.05	Li	0.03	Pb	0.04
Ca	0.08	Mg	0.04	Pt	0.01
Co	0.02	Mn	0.01	Sn	0.10
Cr	0.04	Mo	0.01	Sr	0.01
Cu	0.01	Na	0.04	Ti	0.03
Fe	0.09	Ni	0.03	V	0.01
K	0.05	P	0.11	Zn	0.03

Determination of additional elements is possible if they are not volatilized during the ashing step and do not form insoluble sulfates. Two different reagents are used in sample preparation, depending upon the sample matrix.

Alternatively, some of the elements listed above may be analyzed by Atomic Absorption Spectroscopy (AAS). See UOP Method 391, “Trace Metals in Petroleum Products or Organics by AAS,” for specific metals and their range of quantitation. Metals known to be non-volatile may be analyzed by UOP Method 407, “Trace Metals in Organics by Dry Ashing - ICP-OES.”

References

ASTM Method D1193, “Specification for Reagent Water,” www.astm.org

ASTM Practice D7455, “Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis,” www.astm.org

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UOP Method 391, "Trace Metals in Petroleum Products or Organics by AAS," www.astm.org

UOP Method 407, "Trace Metals in Organics by Dry Ashing - ICP-OES," www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The sample is treated to reduce the volatility of the metals, then coked and ashed. The residue is treated with aqua regia and, after evaporation, is dissolved in acids. Scandium is added as an internal standard. The concentrations of elements in the resulting solutions are determined by ICP-OES.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, laboratory, readable to 0.01 g

Beaker, quartz, low form, 250-mL, Ace Glass, Inc., Cat. No. 5334-14

Bottles, polypropylene, narrow mouth, screw cap, 1000-mL, VWR, Cat. No. 16067-124, several required

Bottle, wash, VWR, Cat. No. 89094-606, for deionized water

Cylinders, graduated, Class B, 5-, 10-, 25-, and 100-mL, VWR, Cat. Nos. 14201-610, -462, -364, and -718, respectively

Flasks, volumetric, Class A, 10-, 50-, and 1000-mL, VWR, Cat. Nos. 89000-398, -402, and -412, respectively

Flasks, volumetric, polypropylene, 25-, 50-, 100-, and 1000-mL, VWR, Cat. Nos. 83008-964, 29615-019, -007, and -062, respectively

Furnace, muffle, capable of operation at 600 °C, VWR, Cat. No. 30604-158

Hot plate, variable heat, maximum operating temperature 510 °C, VWR, Cat. No. 82026-752

Pipet, measuring (Mohr), 5-mL, VWR, Cat. No. 89003-458

Pipets, volumetric, Class A, 1-, 2-, 5-, 10-, 20-, 25-, 50-, and 100-mL, VWR, Cat. Nos. 89003-340, -342, -348, -350, -364, -362, -366-, and -368, respectively

Pipet filler, VWR, Cat. No. 53497-053

Regulator, argon, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Spectrometer, ICP-OES, computer controlled, having sufficient resolving power and dispersion to separate the analytical lines in the 160 to 800 nm region. The data system shall be capable of performing background corrections, blank corrections, mass/volume corrections and dilution corrections. A commercial grating spectrometer with a band pass of 0.018 nm or less in the first order is satisfactory. PerkinElmer, Optima 7300 DV.

Stirring rods, quartz, JSRitter, Cat. No. 21-905

Tongs, beaker, VWR, Cat. No. 82027-374

Watch glasses, quartz, ribbed, 75-mm diameter, Wilmad-LabGlass, Cat. No. C-9990-75, several required

Reagents and Materials

References to catalogue numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. Unless otherwise specified, references to water mean deionized water.

Aqua regia. To prepare, mix 1 mL of concentrated nitric acid with 3 mL of concentrated hydrochloric acid. Prepare a fresh batch each time it is needed.

Argon, 99.995% minimum purity

Cleaning compound, Alconox detergent, VWR, Cat. No. 21835-032

Gloves, neoprene/natural rubber, VWR, Cat. No. 32917-206 (for size large)

Hydrochloric acid, concentrated, trace metals grade, VWR, Cat. No. EM-HX0608-2

Hydrofluoric acid, concentrated, trace metals grade, VWR, Cat. No. EM-HX0628-7, if needed, see *Procedure, Sample Preparation, Ashing*, Step 8

Nitric acid, concentrated, trace metals grade, VWR, Cat. No. EM-NX0408-2

Pipet, dropping, VWR, Cat. No. 52950-206

Scandium metal solution, aqueous, 1000- $\mu\text{g/mL}$, SPEX Certiprep, Inc., Cat. No. PLSC-2, for use as internal standard

Scandium metal solution, aqueous, 100- $\mu\text{g/mL}$. To prepare 50 mL, pipet 5.0 mL of the 1000- $\mu\text{g/mL}$ scandium metal solution into a 50-mL volumetric flask. Fill to the mark with deionized water. Cap and invert several times to mix. The solution should remain stable for one month.

Scandium internal standard, 10- $\mu\text{g/mL}$. To prepare 1000 mL, pipet 10.0 mL of 1000- $\mu\text{g/mL}$ scandium metal solution into a 1000-mL volumetric flask. Fill to the volume mark with water and mix. Store in a 1000-mL polypropylene bottle. The solution should remain stable for one month.

Scandium internal standard, 1- $\mu\text{g/mL}$. To prepare 1000 mL, pipet 1.0 mL of 1000- $\mu\text{g/mL}$ scandium metal solution into a 1000-mL volumetric flask. Using a graduated cylinder, add 100 mL of concentrated hydrochloric acid. Fill to the volume mark with water and mix. Store in a 1000-mL polypropylene bottle. The solution should remain stable for one month.

Standard metal solutions, Al, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Sn, Sr, Ti, V, and Zn solutions of 1000- $\mu\text{g/mL}$ concentrations, SPEX Certiprep, Inc., Cat. Nos. PLAL2-2, PLCA2-2, PLCO2-2, PLCR2-2, PLCU2-2, PLFE2-2, PLK2-2, PLLI2-2, PLMG2-2, PLMN2-2, PLMO2-2, PLNA2-2, PLNI2-2, PLP2-2, PLPB2-2, PLPD2-2, PLPT2-2, PLSN2-2, PLSR2-2, PLTI2-2, PLV2-2, and PLZN2-2, respectively

Sulfuric acid, concentrated, trace metals grade, VWR, Cat. No. EM-SX1248-6, if needed, see *Procedure, Sample Preparation, Ashing*, Step 7

Sulfur trioxide pyridine complex, [26412-87-3], Sigma-Aldrich, Cat. No. S7556, or Acros Organics, Cat. No. 13287-1000

Vials, autosampler, 15-mL, PerkinElmer, Cat. No. B0193233

Water, deionized, ASTM D1193 Type III reagent grade water, unless otherwise specified

Water, hot, tap

The following materials are not required to perform the analyses described herein and are not cited in the *Procedure* portion of the method. However, they may be useful for reference purposes, for

verification of instrument performance, or as an aid in instrument maintenance. The diluted multi-element standard was used to develop part of the precision statement.

Element Blank Oil, 75 viscosity, Conostan Division, SCP Science

Wear Metal Multi-Element Standard, 500- $\mu\text{g/g}$ (mg/kg) each, AccuStandard, Cat. No. WM-21-50X-8. Dilute by weight in Element Blank Oil to 5 mg/kg .

Preparation of Standards

The analyst is expected to be familiar with general laboratory practices. Dispose of all materials in an environmentally safe manner according to local regulations.

CAUTION: All subsequent steps involving additions of reagents and heating of samples must be performed in a properly operating fume hood, and appropriate personal protective equipment must be used. See the MSDS and any local requirements for each material used.

Standards are required for each element to be determined. They are prepared to contain a number of elements with compatible chemistries and no overlap of emission lines. Stock standard solutions are prepared first, from which lower level, matrix-matched, calibration standard solutions are then prepared.

- Calibration standards (including the blank), as well as the final sample preparation, contain the internal standard scandium at a concentration of 1 $\mu\text{g/mL}$

Preparation of Stock Standard Solutions

Prepare stock standard solutions of 100- $\mu\text{g/mL}$ concentration of each element as follows:

1. Pipet 100 mL each of the Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, and Ni 1000- $\mu\text{g/mL}$ commercial stock standards into a 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard A.
2. Pipet 100 mL each of the Sn, Pd, Pt, V, and Zn 1000- $\mu\text{g/mL}$ commercial stock standards into a second 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard B.
3. Pipet 100 mL each of the Mo, P, and Ti 1000- $\mu\text{g/mL}$ commercial stock standards into a third 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard C.
4. Pipet 100 mL each of the K and Na, 40 mL of the Li, and 20 mL of the Sr 1000- $\mu\text{g/mL}$ commercial stock standards into a fourth 1000-mL polypropylene volumetric flask. Dilute to the mark with deionized water. Label as Stock Standard D.
 - Use only 40 mL of Li and 20 mL of Sr because the instrument is more sensitive to these elements. Their concentrations in the stock standard solutions are 40 $\mu\text{g/mL}$ and 20 $\mu\text{g/mL}$, respectively.

Preparation of Blank and Calibration Standard Solutions

Sample preparation differs depending upon the composition of the sample. Lighter materials, kerosene, diesel, atmospheric gas oil, vacuum gas oil, and fatty acid derivatives, are prepared using *Preparation A*. These materials are typically lower in metals. Heavier materials, vacuum tower bottoms, crude, asphalt, and pyrolysis oil, are prepared using *Preparation B*. These materials are typically higher in metals. Blank and Calibration Standard Solutions must be matrix-matched to the sample preparation technique. *Preparation A* is used for metals stabilized with sulfur trioxide pyridine complex. *Preparation B* is used for metals stabilized with sulfuric acid.

Prepare 100 mL of matrix-matched Calibration Standards and a Blank as follows:

1. For use with samples prepared by *Preparation A*: Weigh and add 0.5 ± 0.05 g of sulfur trioxide pyridine complex to each of five cleaned (see *Procedure, Cleaning of Quartz Beakers*) 250-mL quartz beakers. Heat on a hot plate to dryness; the material will melt and then ash. Proceed to Step 3.
2. For use with samples prepared by *Preparation B*: Using a graduated cylinder, add 8 mL of sulfuric acid to each of five cleaned (see *Procedure, Cleaning of Quartz Beakers*) 250-mL quartz beakers. Cover each of the beakers with a watch glass. Heat on a hot plate to dryness. Proceed to Step 3.
3. Place the covered beakers in the muffle furnace at 538 °C for one hour. Cool to ambient temperature and then uncover.
4. Using a graduated cylinder, add 4 mL of aqua regia to the mineral residue in each beaker and evaporate to near dryness on a hot plate. Cool to ambient temperature.
5. Using a graduated cylinder, add 10 mL of hydrochloric acid to each beaker and heat to dissolve any residue. When dissolved, cool to ambient temperature.
6. Quantitatively transfer the contents of each beaker with deionized water into separate 100-mL polypropylene volumetric flasks. Label the five flasks 10-mg/kg Calibration Standard A, B, C, D, and Blank.
7. Pipet into each of the five flasks 1.0 mL of the 100- μ g/mL scandium solution.
8. Pipet 10 mL of Stock Standard A into the flask labeled 10-mg/kg Calibration Standard A. Fill to the mark with deionized water. Follow the same procedure for Standards B, C, and D. The standards contain 10 μ g/mL of their respective elements, except for 4 μ g/mL of Li and 2 μ g/mL of Sr. Fill the flask labeled Blank to the mark with deionized water. The solutions should remain stable for one month.

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of ICP-OES, and the equipment being used. Additional information regarding sample preparation may be found in ASTM Practice D7455, "Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis."

CAUTION: All subsequent steps involving additions of reagents and heating of samples must be performed in a properly operating fume hood, and appropriate personal protective equipment must be used. See the MSDS and any local requirements for each material used.

Cleaning of Quartz Beakers

Clean the 250-mL quartz beakers before each use as follows:

1. Wash the beakers with cleaning compound and rinse with deionized water. Rinse the watch glasses with deionized water.
2. Using a graduated cylinder, add 10 mL of concentrated hydrochloric acid to each beaker, bring to boiling on a hot plate and rinse again 4 to 5 times with deionized water. Dry on a warm hot plate, and allow to cool to ambient temperature.
3. Use the same day.

Sample Preparation, Ashing

Sample preparation differs depending upon the composition of the sample. Lighter materials, kerosene, diesel, atmospheric gas oil, vacuum gas oil, and fatty acid derivatives, are prepared using *Preparation A*. These materials are typically lower in metals. Heavier materials, vacuum tower bottoms, crude, asphalt, and pyrolysis oil, are prepared using *Preparation B*. These materials are typically higher in metals.

Preparation A, Using Sulfur Trioxide Pyridine Complex

CAUTION: All handling of reagents is to be performed in a hood. Use proper PPE and lower the hood shield for protection.

1. Weigh into a cleaned, quartz beaker, to the nearest 0.01 g, an amount of sample appropriate to sample type and the expected metals concentration, typically 20 to 100 g. If the concentrations of the metals are not known, start with 40 g.
 - Ensure that a representative sample is obtained. Viscous samples may be heated until they flow freely. Hot tap water is generally satisfactory, however, more viscous samples may require use of a hot plate. Shake the warmed samples vigorously or stir with a quartz rod and then weigh a sample for analysis to the nearest 0.01 g.
2. Add 0.5 ± 0.05 g of sulfur trioxide pyridine complex and swirl or stir to dissolve. Cover the beaker with a watch glass.
 - The solution may remain cloudy after the sulfur trioxide pyridine complex is dissolved.
3. Place the covered beaker on a hot plate at ambient temperature. Slowly apply heat. A slow increase in heating rate is necessary to avoid loss of sample by “spitting” and will generally require about eight hours before the maximum temperature of the hot plate (~ 500 °C) is reached. If necessary, use a quartz stirring rod to break up any large pieces of char. Leave the stirring rod resting in the spout of the beaker so that the watch glass can provide maximum coverage.
 - To avoid loss of sample, leave the stirring rod in the beaker until it is rinsed in Step 5.
4. After fuming has ceased and the oil is completely charred, place the covered beaker and stirring rod, if used, inside a muffle furnace at 538 °C for 4 to 8 hours (until all carbon is burned off). Remove the covered beaker (with the stirring rod) from the furnace. Cool to ambient temperature and uncover.
 - Do not exceed 538 °C. Loss of some of the more volatile elements may occur.
5. Proceed to *Final Sample Preparation*.

Preparation B, Using Concentrated Sulfuric Acid

CAUTION: A vigorous reaction may occur upon addition of sulfuric acid. All handling of sulfuric acid is to be performed in a hood. Use proper PPE and lower the hood shield for protection.

1. Weigh into a cleaned quartz beaker, to the nearest 0.01 g, an amount of sample appropriate to sample type, typically 5 to 10 g. Cover the beaker with a watch glass.
 - Ensure that a representative sample is obtained. Viscous samples may be heated until they flow freely. Hot tap water is generally satisfactory, however, more viscous samples may require use of a hot plate. Shake the warmed samples vigorously or stir with a quartz rod and then weigh a sample for analysis to the nearest 0.01 g.
2. For samples which may contain water, e.g., pyrolysis oil, place the covered beaker on a hot plate at ambient temperature. Start raising the temperature of the hot plate slowly to vaporize the water. Allow to cool to ambient temperature.

3. Measure out a 2-mL aliquot of sulfuric acid. Use a dropping pipet to add sulfuric acid dropwise to the beaker until any vigorous reaction subsides and foaming ceases.
 - Insert the dropping pipet between the watch glass and the beaker at the spout of the beaker, in order to contain the reaction.
 - The 2-mL aliquot is appropriate for use with up to 10 g of sample. Use proportionately more sulfuric acid for larger sample sizes.
4. After the reaction has subsided, add the remaining sulfuric acid to the sample by inserting the pipet between the watch glass and the beaker at the spout.
 - The balance of the acid may be added more rapidly if the reaction and foaming have subsided.
5. After the acid has been added and the foaming has subsided, place the covered beaker on a hot plate at ambient temperature. Slowly apply heat. A slow increase in heating rate is necessary to avoid loss of sample by “spitting” and will generally require about 12 hours before the maximum temperature of the hot plate (~500 °C) is reached. If necessary, use a quartz stirring rod to break up any large pieces of char. Leave the stirring rod resting in the spout of the beaker so that the watch glass can provide maximum coverage.
 - To avoid loss of sample, leave the stirring rod in the beaker until it is rinsed in Step 7.
6. After fuming has ceased and the oil is completely charred, place the covered beaker and stirring rod, if used, inside a muffle furnace at 538 °C until all carbon is burned off. Remove the covered beaker (with the stirring rod) from the furnace. Cool to ambient temperature and uncover.
 - Do not exceed 538 °C. Loss of some of the more volatile elements may occur.
7. Proceed to *Final Sample Preparation*.

Final Sample Preparation

The final dissolution procedure depends upon the amount of material remaining after ashing. Light samples will typically have only a very small amount of ash remaining, which can easily be dissolved. Heavier samples tend to be higher in metals and have more material remaining after ashing. The amount of material left in the beaker after ashing will determine the amount of acid needed and therefore the final dilution volume.

- Since sulfuric acid is viscous, the final acid concentration should not exceed 5% for aspiration into the instrument.
1. Rinse the sides of the beaker and stirring rod, if used, with approximately 1 mL of deionized water. Add 4 mL of aqua regia and swirl to mix. If the sample is completely dissolved, place the beaker on a hot plate and evaporate to near dryness. Remove from the hot plate and allow to cool to ambient temperature. Proceed to Step 3.
 - Aqua regia must be freshly prepared before each use. Typically, the acids are measured into a 5-mL graduated cylinder just prior to use.
 2. If the sample is not completely dissolved, place the beaker on a hot plate and evaporate to near dryness, allow to cool, add another 4 mL of aqua regia and swirl to mix. If the sample is now completely dissolved, place the beaker on a hot plate and reevaporate to near dryness. Remove from the hot plate and allow to cool to ambient temperature. Proceed to Step 3. If the sample is still not completely dissolved, proceed to Step 4.
 3. Use a pipet to add 10 mL of 1-μg/mL scandium internal standard solution to the beaker. Warm the solution and transfer the solution to a 15-mL autosampler vial for analysis. Proceed to *Spectrophotometric Procedure*.

- For calculation purposes, this is a 10 mL final dilution volume.
4. If undissolved material still remains, add 1.25, 2.5, or 5 mL (See Table 2) of concentrated sulfuric acid, depending upon the amount of undissolved material. Warm on a hot plate to dissolve. Continue heating until sulfuric acid fumes appear. Cool to ambient temperature. If the sample is now completely dissolved, proceed to Step 7.
 - For most samples, this step should not be necessary. If this step is performed, matrix matched standards, including sulfuric acid, must be prepared and used.
 - The undissolved material is left over from the ashing step. This ash usually indicates a higher metals level.
 5. If a jelly-like clump still remains, it is likely silica. Remove the watch glass. Wash down the stirring rod with a small amount of deionized water and remove. Add two drops of hydrofluoric acid. If the sample is now completely dissolved, proceed to Step 7. Additional matrix matching for hydrofluoric acid is not necessary.
 - Do not use glass volumetric flasks with hydrofluoric acid as it will attack the glass and result in a higher metals analysis.
 6. If undissolved material still remains, the sample most likely contains platinum. Add 2 mL of hydrochloric acid and swirl to mix.
 7. Use a pipet to add the amount of 10- μ g/mL scandium internal standard solution shown in Table 2 to the beaker. Warm the solution; some evaporation will occur.

Table 2
Volumes Based Upon Amount of Acid Used

<u>Concentrated sulfuric acid added, mL</u>	<u>10-μg/mL scandium internal standard solution added, mL</u>	<u>Final dilution volume, mL (Volumetric flask used)</u>
1.25	2.5	25
2.5	5.0	50
5.0	10.0	100

8. Quantitatively transfer the digest solution with deionized water to the size of volumetric flask shown in Table 2. Dilute to volume with deionized water. Proceed to *Spectrophotometric Procedure*.

Preparation of Spectrometer

Start up the ICP-OES and ignite the plasma according to the manufacturer's recommendations. Allow a minimum of 30 minutes for warm up after the plasma is ignited before starting the analysis. Using the recommended elemental emission wavelengths, calibrate the spectrometer prior to the analysis of the sample solution. Perform a wavelength calibration prior to the start of the analysis if recommended by the manufacturer. Aspirate the standards and blank to establish the calibration for each element to be measured prior to aspiration of the samples. Table 3 lists recommended wavelengths to be used for the analyses.

- Other wavelengths may be used if there is overlap in transmission lines for the elements analyzed. The alternative wavelengths must retain sufficient sensitivity to achieve the necessary limits of detection.

Spectrometric Procedure

1. Prepare the spectrometer as described under *Preparation of Spectrometer*.
2. Enter the appropriate mass of the sample taken and the final dilution volume for each sample into the data system.

3. Aspirate the blank, the standards, and the samples. The data system will calculate the mg/kg metal in the original sample and print the result.
4. If the concentration of one or more elements in the sample is above the concentration in the calibration standard, dilute the sample with the 1-mg/kg scandium internal standard solution to bring it into a reading range of the standards. Then repeat Steps 2 and 3.

Table 3
Recommended Wavelengths for each Element

<u>Element</u>	<u>Concentration Range in Sample, mg/kg*</u>	<u>λ, nm</u>	<u>Element</u>	<u>Concentration Range in Sample, mg/kg*</u>	<u>λ, nm</u>
Al	0.05-500	396.152	Na	0.04-500	589.592
Ca (low)	0.08-5	393.366	Ni	0.03-100	231.604
Ca (high)	5.0-500	422.673	P	0.11-500	213.618
Co	0.02-200	228.616			Or
Cr	0.04-50	206.149			214.914
Cu	0.01-200	324.754	Pb	0.04-100	220.353
Fe	0.09-200	238.204	Pd	0.05-200	340.458
K	0.05-500	766.491	Pt	0.01-200	265.945
Li	0.03-200	610.364	Sc	internal standard	424.683
		or	Sn	0.10-200	189.989
		670.781	Sr	0.01-200	407.771
Mg	0.04-200	279.553	Ti	0.03-200	334.941
Mn	0.01-200	257.610	V	0.01-200	292.402
Mo	0.01-50	202.030	Zn	0.03-200	206.200

* Based on an ashed 50-g sample, diluted to 50 mL for the higher concentrations and to 10 mL for the lower concentrations.

Calculations

Calculations are normally performed by the computer data reduction software after the analyst enters the appropriate values for the mass of the sample taken and the dilution volume.

The equivalent manual calculation is shown in Equation 1.

$$\text{Concentration of a specific element in original sample, mg/kg} = \frac{RV}{W} \quad (1)$$

where:

R = concentration of element in diluted sample, from instrument readout, $\mu\text{g/mL}$

V = final dilution volume, mL

W = mass of sample used, g

The data system, using known dilutions and concentration levels, determines the correct number of significant figures to report. In general, results are reported to the nearest 0.01 mg/kg, but not exceeding three significant figures.

Note

No palladium standards in an organic matrix were available to use in determining the limit of quantitation or the precision for this element using *Preparation A*. The limit of quantitation of palladium is expected to be similar to that of platinum, depending upon interferences.

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Site Precision, Preparation A

Three samples were analyzed in one laboratory by two analysts. Each analyst carried out tests on two separate days, performing two tests on each sample each day. The precision data are summarized in Table 4.

Table 4
Repeatability and Site Precision, Sample Preparation A, mg/kg

<u>Element</u>	<u>Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Al	0.04	0.005	0.02	0.006	0.03
Al	0.28	0.006	0.02	0.012	0.06
Al	2.79	0.018	0.07	0.019	0.09
Ca	0.06	0.009	0.03	0.022	0.09
Ca	0.32	0.013	0.05	0.035	0.14
Ca	2.97	0.068	0.27	0.055	0.22
Co	0.06	0.001	0.01	0.001	0.01
Co	0.28	0.006	0.02	0.005	0.02
Co	2.76	0.017	0.07	0.018	0.07
Cr	0.03	0.002	0.01	0.003	0.02
Cr	0.27	0.007	0.03	0.018	0.07
Cr	2.81	0.023	0.09	0.026	0.10
Cu	0.01	0.001	0.01	0.005	0.02
Cu	0.24	0.003	0.01	0.005	0.02
Cu	2.68	0.077	0.30	0.081	0.32
Fe	0.05	0.009	0.04	0.010	0.06
Fe	0.30	0.012	0.05	0.038	0.23
Fe	2.89	0.032	0.12	0.057	0.35
K	0.03	0.004	0.02	0.011	0.07
K	0.24	0.009	0.03	0.026	0.16
K	2.90	0.044	0.17	0.115	0.70
Li	0.04	0.001	0.01	0.002	0.01
Li	0.39	0.007	0.03	0.010	0.04
Li	2.64	0.011	0.04	0.016	0.07
Mg	0.03	0.005	0.02	0.004	0.01
Mg	0.27	0.005	0.02	0.005	0.02
Mg	2.78	0.013	0.05	0.010	0.04
Mn	0.03	0.001	0.01	0.001	0.01
Mn	0.28	0.002	0.01	0.003	0.01
Mn	2.80	0.011	0.04	0.008	0.03
Mo	0.03	0.002	0.01	0.001	0.01
Mo	0.27	0.002	0.01	0.002	0.01
Mo	2.74	0.022	0.09	0.032	0.20
Na	0.05	0.017	0.07	0.025	0.15
Na	0.29	0.004	0.01	0.038	0.23
Na	3.00	0.136	0.54	0.171	1.04
Ni	0.02	0.004	0.02	0.006	0.03
Ni	0.27	0.002	0.01	0.007	0.04

<u>Element</u>	<u>Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Ni	2.81	0.014	0.05	0.017	0.10
P	0.07	0.007	0.03	0.014	0.06
P	0.26	0.022	0.09	0.021	0.09
P	2.59	0.058	0.23	0.138	0.62
Pb	0.02	0.003	0.01	0.003	0.01
Pb	0.26	0.010	0.04	0.012	0.05
Pb	2.69	0.042	0.16	0.042	0.16
Pt	0.04	0.001	0.01	0.007	0.03
Pt	0.29	0.013	0.05	0.019	0.08
Pt	2.40	0.112	0.44	0.216	0.85
Sn	0.16	0.023	0.09	0.024	0.11
Sn	2.71	0.041	0.16	0.163	0.73
Sr	0.05	0.001	0.01	0.003	0.02
Sr	0.57	0.005	0.02	0.035	0.21
Sr	2.79	0.020	0.08	0.210	1.28
Ti	0.03	0.001	0.00	0.002	0.01
Ti	0.27	0.005	0.02	0.005	0.02
Ti	2.70	0.016	0.06	0.021	0.08
V	0.03	0.001	0.01	0.001	0.01
V	0.27	0.002	0.01	0.002	0.01
V	2.74	0.022	0.09	0.026	0.12
Zn	0.03	0.003	0.01	0.004	0.03
Zn	0.28	0.005	0.02	0.008	0.05
Zn	2.82	0.013	0.05	0.018	0.11

Repeatability and Site Precision, Preparation B

A sample was analyzed in one laboratory by two analysts. The analysts carried out tests on two separate days, performing two tests on each sample each day. The precision data are summarized in Table 5.

Table 5
Repeatability and Site Precision, Sample Preparation B, mg/kg

<u>Element</u>	<u>Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Al	9.83	0.030	0.12	0.031	0.14

<u>Element</u>	<u>Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Ca	10.06	0.022	0.09	0.051	0.31
Co	9.87	0.033	0.15	0.047	0.19
Cr	9.79	0.113	0.51	0.152	0.60
Cu	9.74	0.072	0.32	0.101	0.40
Fe	9.94	0.039	0.17	0.055	0.21
K	4.93	0.040	0.15	0.047	0.21
Li	4.99	0.005	0.02	0.015	0.05
Mg	9.68	0.073	0.30	0.077	0.33
Mn	9.90	0.028	0.13	0.032	0.13
Mo	9.87	0.097	0.43	0.111	0.44
Na	10.14	0.184	0.80	0.204	0.83
Ni	9.83	0.013	0.05	0.015	0.07
P	5.00	0.039	0.17	0.058	0.26
Pb	4.88	0.055	0.22	0.143	0.64
Pd	9.57	0.072	0.32	0.092	0.36
Pt	5.00	0.015	0.07	0.019	0.09
Ti	9.82	0.112	0.50	0.138	0.54
V	9.93	0.024	0.09	0.034	0.15
Zn	9.75	0.037	0.14	0.039	0.18

Two tests performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Tables 4 and 5 are short-term estimates of repeatability and intermediate precision. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term intermediate precision.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is approximately 28 hours, depending upon sample preparation. The labor requirement for one analysis is 2 hours. In groups of 5 or more samples, the labor requirement for each analysis is 1.5 hours.

Suggested Suppliers

AccuStandard, 125 Market St., New Haven, CT 06513, USA, 1-203-786-5290,
www.accustandard.com

Ace Glass, Inc., P.O. Box 688, 1430 North West Blvd., Vineland, NJ 08362-0688, USA, 1-856-691-3333, www.aceglass.com

Acros Organics, Fisher Scientific, 300 Industry Dr., Pittsburgh, PA 15275, USA, 1-412-490-8300, www.fishersci.com

Conostan Division, SCP Science, 21800 Clark Graham, Baie D'Urfé, QC, Canada H9X 4B6, 1-514-457-0701, www.scpscience.com

JSRitter, 50 Cove St., Portland, ME 04101, USA, 1-207-772-3822, www.jsritter.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA, 1-215-641-2700,
www.mathesontrigas.com

PerkinElmer Analytical Instruments, 710 Bridgeport Ave., Shelton, CT 06484-4794, USA, 1-203-
925-4600, www.perkinelmer.com

Sigma-Aldrich, 3050 Spruce St., St. Louis, MO 63103, USA, 1-314-771-5765, www.sigma-aldrich.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840, USA, 1-732-549-7144,
www.spexcsp.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

Wilmad-LabGlass, 1002 Harding Hwy., Buena, NJ 08310, USA, 1-856-697-3000, www.wilmad-labglass.com